Indian J. Phys. **52A**, 463-468 (1978)

XPS studies of the charging effects for the non-conducting rare-earth oxides

B. D PADALIA

Department of Physics, Indian Institute of Technology, Bombay-400076

AND

W C LANG

Department of Metallurgy, University of Strathclyde Glasgow, U K

X-ray induced photoemission studies (XPS) of the bulk oxides of the heavy rare-earth elements were made using a Vacuum Generator's ESCA 3 instrument equipped with a $X-Y$ plotter and Mg K_α and Al K_α radiation sources Charging effects on the core-level binding energies of Tb_4O_7, Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3 and Lu_2O_3 are determined It is found that the charging of the sample is dependent on the sample thickness and also on the radiation source used to probe the sample. The charging of the samples is estimated with respect to $4f_{7/2}$ peak for clean gold metal at 83·7 eV. The oxygen 1*S* and carbon 1*S* peaks were also monitored These results on bulk oxides are compared with the surface oxides reported by the authors elsewhere

1 INTRODUCTION

X-ray induced photoelectron spectroscopy is a powerful tool for studying the binding energies in solids (Siegbahn *et al* 1967). For non-conducting solids, a knowledge of charging effects is necessary for obtaining accurate values of binding energies (Johansson *et al* 1973) Recently, we reported the core-electron binding energies for the lanthanides (Lang *et al* 1974, 1975, Padalia *et al* (1976, 1977)) In this paper, we present the results of our measurements of the charging effects on the sesquioxides of terbium to lutetium

2 EXPERIMENTAL

Photoemission spectra of the heavy rare earth oxides were measured using a Vacuum Generators ESCA 3 machine equipped with AlK_α and MgK_α radiations as exciting sources. Spectroscopically pure oxide powders supplied by Johnson-Matthey's Ltd ; England were mounted onto the sample-probe using double-sided scotch-tape. The magnitude of charging was estimated by imbedding a piece of gold wire in the powder and recording the gold $4f$ peaks by $X-Y$ plotter Details of the experimental method and the equipment used in this work were described in our previous communications (Lang *et al*1975a, 1975b, Padalia *et al* (1976, 1977)

3. Results and Discussion

Examples of the 4*d* photoemission spectra of the sesquioxides of lutetium, ytterbium and holmium are shown in figures 1–3. The binding energies expressed in eV are referred to the measured Fermi level for the corresponding pure metals. The N_7 ($4f_{7/2}$) peak for gold imbedded in terbium oxide powder together with carbon and oxygen 1*s* signals are presented in figure 4 Photoemission spectra of a blank sellotape and the N_7 peak for a piece of gold fixed on this sellotape are given in figure 6. Spectra recorded using AlK_α and MgK_α radiations are labelled with the alphabets *a* and *b*, respectively. Charging of the samples are estimated with respect to the $4f_{7/2}$ peak for clean gold at 83·7 eV. The values of the charging for the heavy rare-earth oxides are given in table 1.

Table 1 Charging of the samples estimated with respect to $4f_{7/2}$ peak for clean gold metal at 83·7 eV

Samples	*a* (eV)	*b* (eV)
Lu_2O_3	2·0	2·0
Yb_2O_3	2·1	1·9
Tm_2O_3	2·8	2·0
Er_2O_3	2·1	1·5
Ho_2O_3	2·8	1·1
Dy_2O_3	3·6	1·5
Tb_4O_7	3·1	1·9
Sellotape (blank)	0·9	1·0

a—AlK_α radiation *b*—MgK_α radiation.

A scrutiny of the data given in table 1, reveals that the magnitudes of charging, in general are higher for AlK_α than those obtained for MgK_α. This indicates a direct dependence of charging on the penetration power of the radiation used to probe the sample. It is, however not clear why the charging for MgK_α should be more compared to AlK_α in the case of blank sellotape. The measured electron energies for the oxides (figures 1-3) when corrected for the charging effects (table 1), give the actual value of the binding energies. As an example, take the case of lutetium oxide (figure 1). The corrected values of the binding energies for $4d_{5/2}$ and $4d_{3/2}$ are 196·7 eV and 206·4 eV, respectively. The estimated error in the measurement of these energies is found to be $\pm 0{\cdot}4$ eV. The 4*d* spectra of the remaining heavy rare earth oxides (figures 2 and 3) are complex because these exhibit multiplet structure (Lang *et al* 1975).

In our earlier work, it was reported that the evaporated surface oxides of rare earths show no indication of the charging effects (Padalia *et al* (in press)). It is interesting to note that the binding energies of the $4d_{5/2}$ and $4d_{3/2}$ reported

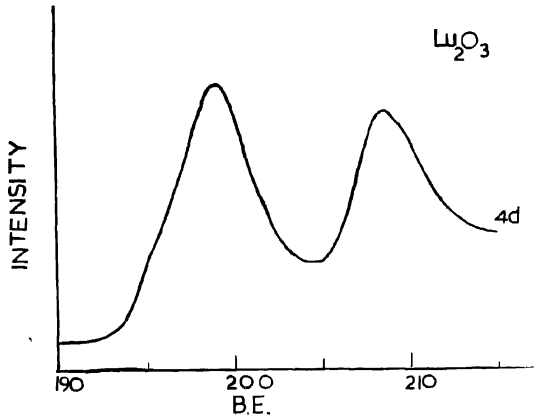

Fig. 1 4*d* Photoemission spectrum of lutetium oxide (Lu_2O_3).

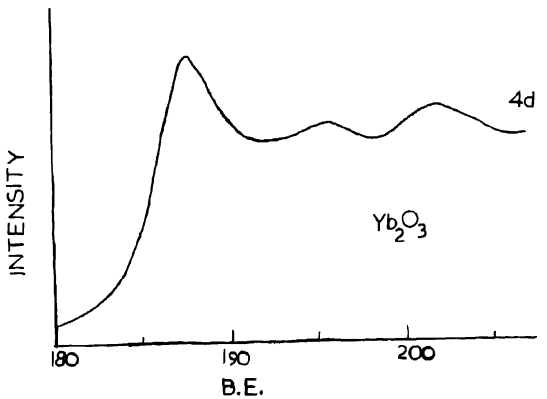

Fig. 2. 4*d* Photoemission spectrum of ytterbium oxide (Yb_2O_3).

for the surface oxide of lutetium are in close agreement with those determined for the bulk oxide of lutetium after applying corrections due to charging.

The effect of film thickness on charging were detected by us previously for the evaporated bulk oxide of rare earths. These samples were prepared by

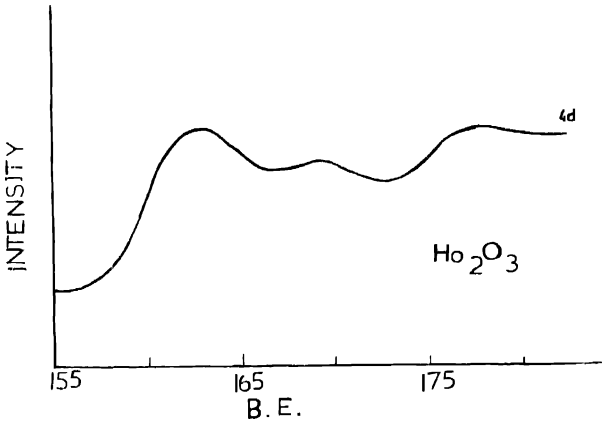

Fig. 3. 4*d* Photoemission spectrum of holmium oxide (Ho_2O_3)

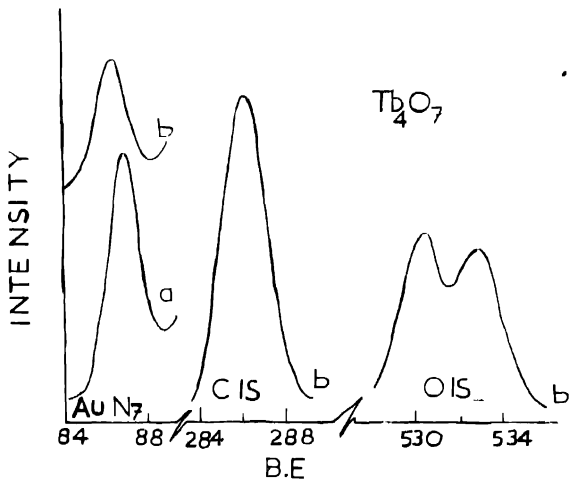

Fig. 4. Carbon and oxygen 1*s* peaks for terbium oxide (Tb_4O_7). $N_7(4f_{7/2})$ peak for gold imbedded in Tb_4O_7. Curves labelled with *a* and *b* corresponding to AlK_α and MgK_α sources, respectively.

evaporating the metal in the presence of oxygen inside a sample preparation chamber maintained at a pressure of 10^{-4} mm of Hg. It was found that the magnitude of charging increases with increasing thickness of the oxide film. In the present case of bulk oxides which were mounted on a sellotape, it is difficult to investigate quantitatively the dependence of charging on the sample thickness. However, the recorded spectra indicate changes in the magnitude of charging with change in the thickness of the sample, using the same radiation as exciting source

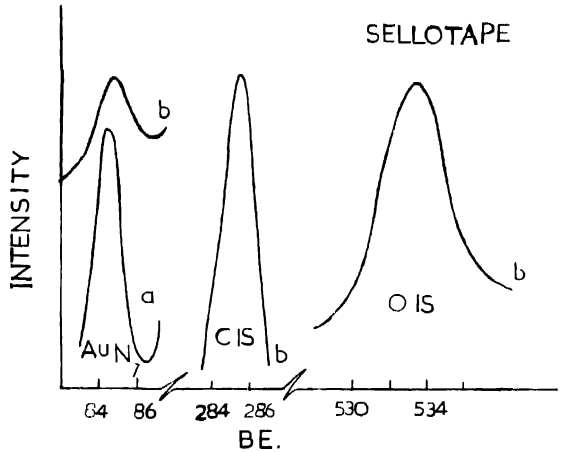

Fig. 5 Carbon and oxygen 1s signals for blank sellotape. N_7 peak for a piece of gold fixed on the sellotape. The curves labelled with *a* and *b* corresponding to AlK_α and MgK_α sources, respectively

The charging effect is also displayed by the photoemission spectra of the oxygen and carbon present in the samples. Since carbon and oxygen spectra exhibit the presence of different species, these cannot be taken as standards for calibration. This fact has also been realized by others in recent years. The gold N_7 peak at 83·7 eV binding energy, however continues to be a reliable standard for calibration. This fact is further supported by the present results.

4. Conclusions

The measured binding energies for the non-conducting materials must be corrected for the charging effects. The charging of the sample is dependent on the radiation source used to probe the sample and also on the sample thickness. The N_7 peak at binding energy 83·7 eV is recommended as a standard for calibration.

Acknowledgments

One of the authors (BDP) expresses his sincere thanks to Dr. D. J. Fabian and Dr. S. Affrossman for extending gracious Scottish hospitability and for providing necessary facilities. Thanks are also due to Dr. L. M. Watson and Mr. Ian Sim for their help and cooperation. Financial assistance from the Science Research Council for Great Britain is gratefully acknowledged.

References

Siegbahn K., Nordling C., Fahlman A., Nordberg R., Hamrin E., Hedman J., Johansson G., Bergmark T., Karlsson S. E., Lingren I. & Lindberg B. 1967 *ESCA–Atomic Molecular and Solid State Structure studied by means of electron spectroscopy*, Nova Acta. Reg. Soc. Sc. Ups Ser IV 20, North Holland Publ Co., Amsterdam.

Johansson G., Hedman J., Berndtsson A., Klasson N. & Nilsson R. 1973 *J. Electr. Spectr.* **2**, 295.

Lang W. C., Padalia B. D., Fabian D. J. & Watson L. M. 1974 *J. Electr. Spectr.* **5**, 207; 1975 **7**, 357.

Lang W. C., Padalia B. D., Watson L. M., Fabian D. J. & Norris P. R. 1975 *Faraday discussion* No. 60, 37.

Padalia B. D., Lang W. C., Norris P. R., Watson L. M. & Fabian D. J. 1977 *Proc. Roy. Society.* **A354**, 269.

Padalia B. D., Gimzewski J. K., Affrossman S., Lang W. C., Waton L. M. & Fabian D. J. 1976 *Surface Science* **61**, 468.